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(54) **RESIN COMPOSITION**

HARZZUSAMMENSETZUNG

COMPOSITION DE RÉSINE

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(56) References cited:

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JP-A- 2012 500 317

US-A1- 2011 315 934

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a resin composition for electrically conductive resin films. More particularly, the present invention relates to a resin composition for electrically conductive resin films which are excellent in tensile elongation, durability to bending and flexibility.

BACKGROUND OF THE INVENTION

[0002] Recently, so-called renewable energy, for example, solar power generation, wind power generation and wave power generation, has attracted attention as new energy sources in place of fossil fuel, such as petroleum, and nuclear power. However, the renewable energy is strongly affected by weather and, therefore, is very unstable in output. When supplying a large amount of the renewable energy to power grids, it is necessary, for example, to provide high-capacity batteries to level the fluctuating output.

[0003] One example of the high-capacity battery is a redox flow battery. The redox flow battery comprises two kinds of ionic solutions which are separated with a cation exchange membrane, in each of which solutions an electrode is placed. At the electrodes, an oxidation reaction and a reduction reaction occur simultaneously to cause charge and discharge. For example, in a redox flow battery in which an aqueous sulfuric acid solution containing vanadium is used at each pole, vanadium (IV) is oxidized to vanadium (V) at the positive pole, and vanadium (III) is reduced to vanadium (II) at the negative pole for the charge. In the discharge, the reverse reactions occur. The redox flow batteries have an advantage that it is easy to provide large-capacity ones. The batteries function at room temperature. Further, no combustible or explosive material is used or generated in the batteries. Therefore, they are very safe compared to sodium-sulfur batteries and lithium ion secondary batteries.

[0004] Electrodes of redox flow batteries are immersed in an electrolyte such as an aqueous sulfuric acid solution. Further, oxidation and reduction reactions occur at the electrodes. Therefore, the electrodes need to have high electric conductivity and chemical resistance. Accordingly, carbon fiber assemblies or platinum plating have been used in the electrodes. However, the carbon fiber assemblies allow a liquid to pass through and, therefore, have a problem that the junction with a copper wire is affected by an aqueous sulfuric acid solution passed through the assemblies. The platinum plating is a very good conductor and is excellent in chemical resistance, but has a drawback that it is of a noble metal and costly.

[0005] Therefore, electrically conductive resin films comprising electrically conductive carbon such as ketjen black have been proposed as the electrodes (see Patent Literature 1 to 4), or electrodes made of carbon fiber assemblies or of copper plates have been coated with the aforesaid electrically conductive resin film. However, when the electrically conductive resin film comprises an adequate amount of electrically conductive carbon to have sufficiently high electric conductivity, the film is very poor in tensile elongation, durability to bending or flexibility and, therefore, easily breaks by a physical force. When the amount of electrically conductive carbon is so small to secure good tensile elongation, durability to bending and flexibility, the volume resistivity of the film exceeds $10\ \Omega\cdot\text{cm}$ to increase internal resistance of a redox flow battery in which the film is used as the electrodes or coatings on the electrodes, which makes the battery unsatisfactory.

[0006] In recent years, carbon nanotubes have attracted attention as conductive carbon and been expected to solve the aforesaid problems (see Patent Literature 5 and Non-Patent Literature 1). However, carbon nanotubes have problems that they are difficult to spread and, therefore, very difficult to be dispersed in resins. Therefore, a large amount of carbon nanotubes must be added, like ketjen black, in order to obtain satisfactorily high electric conductivity and, therefore, the resulting electrically conductive resin film is practically inferior in tensile elongation, durability to bending and flexibility. When high shearing stress is applied in spreading and dispersion steps in order to obtain better spreading and dispersion of carbon nanotubes, the carbon nanotubes break and, therefore, it is again necessary to use a large amount of carbon nanotubes in order to obtain satisfactorily high electric conductivity.

[0007] An electrically conductive film has been proposed, made of a composition obtained by mixing carbon black or carbon nanotubes with propylene-olefin copolymer wax to prepare a master batch which is then mixed with an organic polymer (see Patent Literature 6 and 7). The master batch makes it possible to incorporate carbon black or carbon nanotubes in a large amount into the polymer. However, the electric conductivity of the resulting film is not enough. WO 2011/129215 discloses an electrically conductive composite prepared by mixing a thermoplastic resin, a carbonaceous material selected from graphite and carbon black, and a carbon nanotube, wherein the carbonaceous material content is 20 to 150 parts by weight and the carbon nanotube content is 1 to 10 parts by weight relative to 100 parts by weight of the thermoplastic resin. In a particular embodiment, the carbonaceous material contains at least one graphite selected from the group consisting of expanded-, laminar- and spherical graphite, and at least one carbon black selected from the group consisting of acetylene black and ketjen black. The resin is used for an electrode of a redox flow battery. WO

2006/106609 discloses an electrically conducting curable resin composition comprising (A) a hydrocarbon compound having a plurality of carbon-carbon bonds, such as 1,2-polybutadiene, 3, 4-polyisoprene and a styrene-isoprene copolymer, (B) an elastomer excluding the component (A), and (C) a carbonaceous material which is one or more members selected from natural-, artificial-, expanded graphite, carbon black, carbon fiber, vapor grown carbon fiber, and carbon nanotube.

[0008] US 2011/0315934 describes the preparation of a graphite-vinyl ester resin composite conducting plate which can be used as an electrode of vanadium redox battery. The plate is prepared by compounding vinyl ester resin and graphite powder, the graphite powder content ranging from 70 to 95 wt% based on the total weight of the graphite powder and vinyl ester, wherein 0.01 to 15 wt% functionalized graphene, based on the weight of the vinyl ester resin, is added during the compounding. The compounded material is then molded to the desired shape at 80 to 250 °C.

[0009] JP 2012-500317 discloses a thermoplastic resin composition comprising (A) 50 to 90 wt% polyphenylene sulfide resin; (B) 5 to 30 wt% graphite; (C) 5 to 30 wt% fluoropolyolefin resin; (D) 1 to 10 wt% whiskers; and (E) 0.01 to 10 wt% carbon nanotubes. The resin composition is stated to exhibit electrical conductivity, wear resistance and heat resistance.

[0010] JP 2005-200620 discloses a thermoplastic resin composition comprising a thermoplastic resin, ketjen black or carbon nanotubes and vapor-deposition carbon fibers. The molded product of the thermoplastic resin composition is stated to have good conductivity, mechanical strength, flexibility, durability and surface smoothness.

PRIOR ART LITERATURE

PATENT LITERATURE

[0011]

Patent Literature 1: Japanese Patent Application Laid-Open No. Hei 1-149370/1989

Patent Literature 2: Japanese Patent Application Laid-Open No. Hei 4-259754/1992

Patent Literature 3: Japanese Patent Application Laid-Open No. Hei 7-053813/1995

Patent Literature 4: Japanese Patent Application Laid-Open No. 2001-015144

Patent Literature 5: Japanese Patent Application Laid-Open No. 2006-111870

Patent Literature 6: Japanese Patent National Phase Publication No. 2012-507586

Patent Literature 7: Japanese Patent National Phase Publication No. 2012-507587

NON-PATENT LITERATURE

[0012] Non-Patent Literature 1 : Takase, Hirofumi, "Dispersion Technique and Evaluation of Carbon Nanotubes", Seikei-Kakou, Vol.18, No.9, 2006, pp.646-652

SUMMARY OF THE INVENTION

PURPOSE OF THE INVENTION

[0013] The object of the present invention is to provide a resin composition for an electrically conductive resin film which is excellent in tensile elongation, durability to bending and flexibility and is suitable as electrodes or protective coatings on the electrodes in electrolyte-circulating secondary batteries such as redox flow batteries, zinc-chlorine batteries and zinc-bromine batteries.

MEANS FOR ACHIEVING THE PURPOSE

[0014] The present inventors have found that the aforesaid problems are solved by adding carbon nanotubes together with acetylene black to a thermoplastic resin.

[0015] Thus, the present invention is a resin composition comprising

(A) a thermoplastic resin, and
carbon fillers,

wherein the carbon fillers consist of the following:

(B) carbon nanotubes; and
(C) acetylene black;

and, optionally, also include (D) carbon fiber,
 wherein the amount of component (B) is 1 to 60 parts by weight, relative to 100 parts by weight of component (A); the
 amount of component (C) is 1 to 100 parts by weight, relative to 100 parts by weight of component (A) ; and, when
 present, the amount of component (D) is 1 to 60 parts by weight, relative to 100 parts by weight of component (A).

EFFECTS OF THE INVENTION

[0016] The film made of the present composition has high electric conductivity and is excellent in tensile elongation,
 durability to bending and flexibility and, therefore, can suitably be used as electrodes or protective coatings on the
 electrodes in electrolyte-circulating secondary batteries such as redox flow batteries, zinc-chlorine batteries and zinc-
 bromine batteries.

BRIEF DESCRIPTION ON THE DRAWING

[0017] Fig. 1 is a graph showing the relation between the volume resistivity, ρ , and the tensile elongation, E, of the
 films obtained in the Examples and the Comparative Examples.

EMBODIMENTS OF THE INVENTION

(A) Thermoplastic resin

[0018] Component (A) accommodates components (B) to (D) which are carbon fillers, and provides the resulting film
 with mechanical properties such as tensile elongation, durability to bending and flexibility. Examples of the thermoplastic
 resin include, for example, polyolefin resins such as polyethylene, polypropylene, polybuten-1, poly(4-methylpentene-
 1), chlorinated polyethylene, ethylene- α -olefin copolymers, ethylene-vinyl acetate copolymers, and ethylene-acrylic acid
 ester copolymers; polyvinyl chloride type resins such as polyvinyl chloride and vinyl chloride-vinyl acetate copolymers;
 polyamide type resins such as nylon 11 and nylon 12; polyurethane type resins; non-crystalline, low-crystalline or crys-
 talline polyester type resins; acrylonitrile-butadiene-styrene copolymers (ABS resins); hydrogenated styrene-based elas-
 tomers such as hydrogenated styrene-conjugated diene copolymers; acrylic resins; silicone resins; polyvinylidene chlo-
 ride type resins; and chloroprene resins. These may be appropriately used alone or in a combination of two or more of
 these according to the desired application of the electrically conductive resin film.

[0019] For example, in a case where the resulting electrically conductive resin film is used as electrodes or coatings
 on the electrodes in redox flow batteries in which an aqueous sulfuric acid solution containing vanadium is used at each
 pole, the film needs to be resistant to an aqueous sulfuric acid solution and, therefore, component (A) is preferably
 polyethylenes or chlorinated polyethylenes and, more preferably, chlorinated polyethylenes having a chlorine content
 of 25 to 45 % by weight. In view of a film-forming property in calendering, crystalline chlorinated polyethylenes having
 a chlorine content of 25 to 45 % by weight are most preferred. It is noted that the crystalline chlorinated polyethylenes
 is intended to have melting enthalpy (ΔH) of 20 J/g or more in a second melting curve which is obtained in the final
 heating step of the following measurement program: keeping a sample at 190 degrees C for 5 minutes, cooling to -10
 degrees C at a rate of 10 degrees C/min., keeping at -10 degrees C for 5 minutes and then heating to 190 degrees at
 a rate of 10 degrees C/min. with DSCQ, type 1000, ex TA Instruments Japan. Examples of the crystalline chlorinated
 polyethylenes include ELASLEN 404B (trade name) and ELASLEN 303B (trade name), ex Showa Denko Inc.

(B) Carbon nanotubes

[0020] The carbon nanotubes are fibrous materials in the form of a single-wall tube or of a tube with multiple walls
 coaxially laminated to each other, and have a diameter of approximately 1 to 250 nm and a length of approximately 0.1
 to 250 μ m. The wall is composed of a network of six-membered rings consisting of carbon atoms, i.e., graphene sheet.
 The carbon nanotubes function as an electrically conductive filler to provide the electrically conductive resin film with
 high electric conductivity. Therefore, the carbon nanotubes preferably have less lattice defects and high electric con-
 ductivity. Further, the carbon nanotubes preferably have a small bulk specific gravity so as to be easily spread.

[0021] Commercially available examples of the carbon nanotubes include NanocylINC7000 (trade name, ex Nanocyl
 S.A.) and VGCF-X (trade name, ex Showa Denko Inc.).

[0022] The amount of component (B) is 1 to 60 parts by weight, preferably 20 to 50 parts by weight, relative to 100
 parts by weight of component (A). If the amount is less than the lower limit, the volume resistivity is higher than 10 Ω -
 cm. If the amount is too much, the tensile elongation, the durability or the flexibility may not be enough.

(C) Acetylene black

[0023] Component (C) functions to secure good processability in steps of preparing (melt-kneading) the resin composition and forming a film. It functions also to help spreading and dispersion of carbon nanotubes (B) and, if any, carbon fiber (D), thereby increasing the electric conductivity of the film and improving mechanical properties such as tensile elongation. Further, component (C) itself has good electric conductivity and, therefore, functions to increase the electric conductivity of the film.

[0024] Acetylene black is carbon fine particles produced by pyrolysis of acetylene gas and is electrically conductive carbon black having a partially-graphitized structure. Commercially available examples of acetylene black include DENKA BLACK (trade name, ex Denki Kagaku Kogyo Inc.).

[0025] Besides acetylene black, ketjen black is known as electrically conductive carbon black. Although ketjen black has a high electric conductivity, it has a hollow shell form, unlike acetylene black. Therefore, a composition obtained by kneading ketjen black with a thermoplastic resin and the carbon nanotubes has less ductility in melting in a film-forming step and, therefore, may not be formed into a film.

[0026] Although not included in the scope of the appended claims, graphite is described herein. Graphite, also called black lead, is mineral consisting of carbon atoms. Graphite encompasses natural graphite such as flake graphite and amorphous graphite, and synthetic graphite such as pyrolytic graphite. Ground graphite is described herein which preferably has a mean particle diameter of 10 μm or less, more preferably 5 μm or less. The mean particle diameter is a particle diameter at cumulative 50% by mass in a particle diameter distribution curve obtained with a laser diffraction and scattering type particle diameter analyzer, MT320011 (trade name, ex Nikkiso Co., Ltd.).

[0027] The amount of component (C) is 1 to 100 parts by weight, preferably 10 to 60 parts by weight, more preferably 20 to 50 parts by weight, relative to 100 parts by weight of component (A). If the amount is less than the lower limit, a balance between a volume resistance and a tensile elongation is lower, so that the equation (1) described below is not met. If the amount is too much, the tensile elongation, the durability to bending or the flexibility may not be enough.

(D) Carbon fiber

[0028] Carbon fiber is obtained by heating to carbonize a precursor, organic fiber, and comprises carbon atoms in an amount of 90% by weight or more. Component (D) is an optional component which may be added to provide the film with further electric conductivity.

[0029] Carbon fiber can provide high electric conductivity in an orientation direction of fibers. However, electric conductivity in a direction vertical to the orientation direction is low. Therefore, electric conductivity of a film varies usually greatly depending on measurement positions and directions in the film. Surprisingly, when component (D) is added together with carbon components (B) and (C) to component (A), the aforesaid problem is significantly improved.

[0030] Component (D) preferably has a high electric conductivity in itself. Further, component (D) is preferably cut into a fiber length of approximately 1 to 15 mm so as to be easily melt-kneaded in a step of preparing the resin composition. Commercially available examples of the carbon fiber include Torayca Cut Fiber (trade name, ex Toray Industries, Ltd.).

[0031] The amount of component (D) is 1 to 60 parts by weight, preferably 10 to 30 parts by weight, relative to 100 parts by weight of component (A). If the amount is less than the lower limit, a less effect is attained by component (D). If the amount is too much, the tensile elongation, the durability to bending or the flexibility may not be enough.

[0032] The resin composition may further comprise known additives, such as, for example, lubricants, antioxidants, anti-aging agents, weathering stabilizers such as light stabilizers and UV light absorbers, heat stabilizers, copper inhibitors, release agents, and surfactants, as long as the purpose of the invention is not impeded. The total amount of the additives is 0.001 to 5 parts by weight relative to 100 parts by weight of component (A).

[0033] Further, inorganic fillers other than components (B) to (D) may further be added as long as the purpose of the invention is not impeded. Examples of such inorganic fillers include light calcium carbonate, heavy calcium carbonate, magnesium silicate hydrate and talc. The amount of such inorganic fillers is 1 to 20 parts by weight relative to 100 parts by weight of component (A).

[0034] The present resin composition may be prepared by melt-kneading components (A) to (C) and, if necessary, component (D) and the other optional components with any known melt kneader. Examples of the melt kneader include batch-type kneaders such as pressure kneaders and mixers; kneading extruders such as co-rotating twin-screw extruders and counter-rotating twin-screw extruders; and calender roll kneaders. Any combination of these may also be used. The resulting resin composition may be pelletized in any method and then formed into a film, such as, for example, using a calender machine or a combination of an extruder with a T-die. The pelletization may be carried out in such a method as hot cutting, strand cutting or underwater cutting. Alternatively, the melt-kneaded resin composition may be fed as such to a calender machine or a T-die to be formed into a film. The calender machine may be any one, such as, for example, an upright-type three-roll machine, an upright-type four-roll machine, an L-type four-roll machine, an inverted L-type four-roll machine or a Z-type rolls machine. The extruder may be any one, such as, for example, a single screw

extruder, a co-rotating twin-screw extruder or a counter-rotating twin-screw extruder. The T-die may be any one, such as, for example, a manifold die, a fish-tail die or a coat-hanger die.

[0035] The electrically conductive resin film thus obtained may be crosslinked or cured in any known method, for example, by means of electron beam irradiation, to enhance heat resistance and chemical resistance of the film.

[0036] The electrically conductive resin film comprising the present resin composition has a volume resistivity in $\Omega \cdot \text{cm}$, ρ , measured according to the Japanese Industrial Standards (JIS) K 7194, of $10 \Omega \cdot \text{cm}$ or less and the volume resistivity, ρ , meets the following equation (1):

$$\text{Log } \rho \leq 0.02E - 1.4 \quad (1)$$

wherein E is the tensile elongation in % of the film which is measured according to JIS K 7127.

[0037] In general, electrically conductive resin films need to have a volume resistivity of $10 \Omega \cdot \text{cm}$ or less to be used as electrodes or coatings on the electrodes, for example, in redox flow batteries. The volume resistivity is preferably $1.0 \Omega \cdot \text{cm}$ or less, more preferably $0.1 \Omega \cdot \text{cm}$ or less. The lower the volume resistivity is, the more preferable the film is.

[0038] Further, electrically conductive resin films need to have good mechanical properties such as tensile elongation, durability to bending and flexibility so that electrodes in a form of the films or coatings composed of the films on electrodes are not easily broken by a physical force. Therefore, an electrically conductive film having a lower volume resistivity and higher mechanical properties such as a tensile elongation is more practical and more useful in industrial applications.

[0039] The electrically conductive resin film comprising the present resin composition has a volume resistivity, ρ , of $10 \Omega \cdot \text{cm}$ or less, and meets the equation (1). Therefore, the film may suitably be used as electrodes or protective coatings on the electrodes, for example, in redox flow batteries, zinc-chlorine batteries and zinc-bromine batteries.

[0040] The film meeting the equation (1) has a better balance between the volume resistivity, ρ , and the tensile elongation, E, compared to films not meeting the equation (1). Fig. 1 is a semilog graph showing a relation between the volume resistivity, ρ , and the tensile elongation, E, of the films of the Examples (indicated by the symbol, \circ) and the Comparative Examples (indicated by the symbol, \diamond). In the graph, the ordinate is for ρ , and the abscissa is for E. Line (1) shows the equation, $\text{Log } \rho = 0.02E - 1.4$, and line (2) shows the equation, $\text{Log } \rho = 0.02E - 1.6$. When a film has a lower volume resistivity, ρ , and a higher tensile elongation, E, the film is more preferred as electrodes, for example, in redox flow batteries. Therefore, it can be said that in the graph of Figure 1, the nearer to zero the volume resistivity, ρ , is and the farther from zero in the right direction the tensile elongation, E, is, the better the aforesaid balance is. As seen in Fig. 1, the films of the Examples meet the equation (1), that is, they are on or below the line (1). This means that these films have the superior balance, compared to the films of the Comparative Examples. The better the balance is, the more preferable the film is. It is more preferred that the following equation (2) is met.

$$\text{Log } \rho \leq 0.02E - 1.6 \quad (2)$$

[0041] The volume resistivity, ρ , and the tensile elongation, E, herein are determined by the following method.

(1) Volume resistivity, ρ :

[0042] The volume resistivity was measured by a 4-pin probe method (probe method) according to JIS K 7194. The film was conditioned in a test chamber at a temperature of 23 ± 2 degrees C and a relative humidity of 50 ± 5 % for 24 hours or more, and was cut in a size of 80mm in the machine direction x 50 mm in the width direction to prepare a specimen. The specimen was subjected at its five positions to the measurement using a resistivity meter, Loresta GPMCP-T610 (trade name, ex Mitsubishi Chemical Analytec Co., Ltd.), with a probe having pins linearly arranged at a constant interval of 5mm. This measurement was carried out on three specimens to obtain 15 results of the volume resistivity in total. These values were averaged to determine the volume resistivity, ρ , of the film. A thickness of the film was measured using Dial Thickness Gauge H-1A (trade name, ex Ozaki MFG. Co., Ltd.) according to the dimension measurement of specimens in JIS K 7194. For the method for measuring an electric resistivity and its theory, reference may be made, for example, to the home page of Mitsubishi Chemical Analytec Co., Ltd. (<http://www.mccat.co.jp/3seihin/genri/ghlup2.htm>).

(2) Tensile elongation, E:

[0043] The tensile elongation was measured according to JIS K 7127. The film was conditioned in a test chamber at a temperature of 23 ± 2 degrees C and a relative humidity of 50 ± 5 % for 24 hours or more, and was cut into a form of a specimen type No.1 dumbbell so that the width direction of the film was a tensile direction, and then subjected to a

tensile test under the conditions of the initial distance between chucks of 120mm, the distance between gauge lines of 50mm, and the tensile speed of 5mm/minute to obtain an elongation at break. This test was carried out on five specimens. The results were averaged to determine the tensile elongation, E, of the film. The thickness of the film was determined by measuring a thickness each at ten points between the gauge lines of a specimen, using Dial Thickness Gauge H-1A (trade name, ex Ozaki Mfg. Co., Ltd.) and then averaging the results.

EXAMPLES

[0044] In the following, the present invention will be illustrated by the Examples, but is not limited thereto.

Examples 1 to 11 and Comparative Examples 1 to 14

[0045] The composition consisting of the components in the amount ratio as shown in Table 1 was melt-kneaded using a 5L-volume intensive mixer, ex Nippon Roll MFG. Cp., Ltd. The discharge temperature was 190 degrees C. Then, a film having a thickness of 300 μ m was obtained using an inverted L-type four-roll calender machine having a roll diameter of 200mm and a roll width of 700mm, ex Nippon Roll MFG. Cp., Ltd. The roll temperatures were 205 degrees C, 205 degrees C, 185 degrees C and 175 degrees C for the first roll, the second roll, the third roll and the fourth roll, respectively, and the taking-up speed was 5m/minute. The resulting film was subjected to the measurements of the volume resistivity, ρ , and the tensile elongation, E, and further to the following tests for durability to bending and flexibility. The results are as shown in Table 1.

(3) Durability to bending

[0046] The film was conditioned in a test chamber at a temperature of 23 ± 2 degrees C and a relative humidity of 50 ± 5 % for 24 hours or more, and was cut into a form of specimen type 1B according to JIS K 7127 so that the machine direction of the film was a tensile direction to prepare a specimen. The specimen was folded at an angle of 180 degrees so that the whole parts to be chucked at the ends of the specimen were overlapped with each other, squeezed through fingers and then unfolded. Then, the specimen was folded at an angle of 180 degrees in the opposite direction, squeezed through fingers and then unfolded. These operations as one set were repeated along the one and same crease. The criteria are as follows.

G: The film did not break even after six sets.

M: The film broke in 2 to 6 sets.

B: The film broke in one set.

(4) Flexibility

[0047] The modulus at 5% elongation was determined as a measure of flexibility on the stress-strain curve obtained above in the tensile test in (2). A smaller modulus means that flexibility is higher.

[0048] The materials used were as follows:

Component (A)

[0049]

(A-1): ELASLEN 404B (trade name), chlorinated polyethylene, chlorine content: 40% by mass, melt flow rate (180 degrees C, 211.8N) : 25g/10 min., melting enthalpy: 29J/g, ex Showa Denko Inc.;

(A-2): ELASLEN 303B (trade name), chlorinated polyethylene, chlorine content: 32% by mass, melt flow rate (180 degrees C, 211.8N) : 25g/10 min., melting enthalpy: 50J/g, ex Showa Denko Inc.;

(A-3) D9100.00 (trade name), low density polyethylene, melt flow rate (190 degrees C, 21.18N): 1g/10 min., density: 877kg/m³, ex Dow Chemical;

Component (B)

[0050]

(B-1): Nanocyl NC7000 (trade name), multi-wall carbon nanotube, average diameter: 9.5nm, average length: 1.5 μ m, bulk specific gravity: 0.043g/cm³, purity: 90% by mass, ex Nanocyl S.A.;

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(B-2): VGCF-X (trade name), multi-wall carbon nanotube, average diameter: 15nm, average length: 3 μ m, bulk specific gravity: 0.08g/cm³, purity: 93% by mass, ex Showa Denko Inc.);

(B-3): C100 (trade name), multi-wall carbon nanotube, average diameter: 12nm, average length: 1 μ m, bulk specific gravity: 0.1g/cm³, purity: 90% by mass, ex Arkema Inc.;

Component (C)

[0051] (C-1) : DENKA BLACK Granule (trade name), acetylene black, average diameter of primary particles determined by observation under a transmission electron microscope (TEM): 35nm, specific surface area: 69m²/g; ex Denki Kagaku Kogyo Inc.;

Comparative Component (C)

[0052]

(C-2) : Z-5F (trade name), ground natural graphite, flaky, average diameter: 4 μ m, ex Ito Graphite Co., Ltd.;

(C-3): KJ300 (trade name), ketjen black, ex Lion Corporation;

Component (D)

[0053] (D-1) : Torayca Cut Fiber T008A-006 (trade name), carbon fiber, cut length: 6mm, fiber diameter: 7 μ m, ex Toray Industries, Ltd.;

Optional component

[0054] STANN JF-95B (trade name), stabilizer for chlorinated polyethylene, ex Nitto Kasei Kyogyo Inc.

Table 1-1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6*	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
(A)	100	100	100	100		100	100	100		100	100
(A-1)											
(A-2)					100						
(A-3)									100		
(B)	40	40	25	10	25	25			40	40	30
(B-1)							40				
(B-2)											
(B-3)								25			
(C) Comp.(C)	40	20	40	40	40		40	40	25	60	30
(C-1)						40					
(C-2)											
(C-3)											
(D)	20	20	20	20	20	20	20	20	20		
Optional component	2	2	2	2	2	2	2	2	2	2	2
Evaluation results	0.072	0.088	0.15	3.0	0.17	0.28	0.080	0.26	0.25	0.14	0.35
Volume resistivity, ρ , $\Omega \cdot \text{cm}$	25	33	58	118	77	50	24	47	249	34	96
Tensile elongation, E, %	-1.14	-1.06	-0.82	0.48	-0.77	-0.55	-1.10	-0.59	-0.60	-0.85	-0.46
Logp	-0.90	-0.74	-0.24	0.96	0.14	-0.40	-0.92	-0.46	3.58	-0.72	0.52
0.02E-1.4	-1.10	-0.94	-0.44	0.76	-0.06	-0.60	-1.12	-0.66	3.38	-0.92	0.32
0.02E-1.6	G	G	G	G	G	G	G	G	G	G	G
Durability to bending	14.9	12.7	9.7	7.1	9.9	7.2	15.0	10.1	5.2	10.9	4.7
5% Modulus, Mpa											
* Reference Example is not within scope of appended claims											

Table 1-2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14
(A)	100	100	100	100	100	100	100	100	100	100	100	100	100	100
(A-1)														
(A-2)														
(A-3)														
(B)	120	60	40	35		40	40	35	20				40	40
(B-1)														
(B-2)														
(B-3)														
(C) Comp. (C)					60					60	60	40		
(C-1)														
(C-2)														
(C-3)														
(D)						20	60	35	30	40	60	20	60	40
(D-1)														20
Optional component	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Evaluation results	0.11	0.12	0.25	0.44	32	0.21	0.11	0.24	0.50	14	4.3	0.28	*	*
Volume resistivity, ρ , $\Omega \cdot \text{cm}$														
Tensile elongation, E, %	11	21	22	23	230	20	17	29	35	27	12	16		
Logp	-0.96	-0.92	-0.60	-0.36	1.51	-0.68	-0.96	-0.63	-0.30	1.15	0.63	-0.55		
0.02E-1.4	-1.18	-0.98	-0.96	-0.94	3.20	-1.00	-1.06	-0.82	-0.70	-0.86	-1.16	-1.08		
0.02E-1.6	-1.38	-1.18	-1.16	-1.14	3.00	-1.20	-1.26	-1.02	-0.90	-1.06	-1.36	-1.28		
Durability to bending	B	G	G	G	G	M	B	M	G	G	B	B		
5% Modulus, Mpa	11.8	5.8	3.2	2.8	3.8	10.3	13.8	8.8	6.3	7.1	9.5	19.5		
* No film could be formed.														

[0055] The films of Examples 1 to 11 (Example 6 not within scope of claimed invention) meet the equation (1), and have the low volume resistivity and the high tensile elongations, durability to bending and flexibility. On the other hand, the films of Comparative Examples 1 to 12 do not meet the equation (1), and have at least one of low tensile elongation, durability to bending, flexibility or electric conductivity. In Comparative Examples 13 and 14 where ketjen black was used in place of component (C), the resin compositions had no ductility in melting when subjected to a film-forming operation and, therefore, could not be formed into a film.

[0056] For the film of Example 9, a volume resistivity, ρ , was measured also after the tensile test. The film was cut into a size of 100mm x 25mm, where the width direction of the film was the longitudinal direction of a specimen. A mark was put with a felt pen at the center (intersection of the both diagonals), drawn at a speed of 5mm/minute until the distance between chucks increased from 50mm at the beginning to 100mm. Then the volume resistivity, ρ , was determined only at the one marked position, as mentioned in (1) above. The volume resistivity before the tensile test was $2.5 \times 10^{-1} \Omega \cdot \text{cm}$, while that after the tensile test was $3.6 \times 10^0 \Omega \cdot \text{cm}$. Thus, the tensile deformation of 100% resulted in only one digit increase in volume resistivity. This means that the electrically conductive resin film made of the present resin composition has much less change in electric conductivity under deformation of the film.

Claims

1. A resin composition comprising

(A) a thermoplastic resin, and
carbon fillers,

wherein the carbon fillers consist of the following:

(B) carbon nanotubes; and
(C) acetylene black;

and, optionally, also include (D) carbon fiber,

wherein the amount of component (B) is 1 to 60 parts by weight, relative to 100 parts by weight of component (A); the amount of component (C) is 1 to 100 parts by weight, relative to 100 parts by weight of component (A); and, when present, the amount of component (D) is 1 to 60 parts by weight, relative to 100 parts by weight of component (A).

2. The resin composition according to claim 1, wherein component (A) is at least one selected from the group consisting of polyethylenes and chlorinated polyethylenes.

3. The resin composition according to claim 1 or 2, wherein the composition further includes:

(D) carbon fiber as a carbon filler.

4. The resin composition according to any one of claims 1 to 3, wherein the amount of component (B) is 20 to 60 parts by weight, relative to 100 parts by weight of component (A).

5. The resin composition according to claim 4, wherein the amount of component (B) is 20 to 50 parts by weight, relative to 100 parts by weight of component (A).

6. Use of the resin composition according to any one of claims 1 to 5, wherein the composition is to be used for an electrode of a redox flow battery.

7. An electrically conductive resin film comprising the resin composition according to any one of claims 1 to 5.

8. The electrically conductive resin film according to claim 7, wherein the film has a volume resistivity in $\Omega \cdot \text{cm}$, ρ , measured according to JIS K 7194, of $10 \Omega \cdot \text{cm}$ or less and the volume resistivity, ρ , meets the following equation (1):

$$\text{Log } \rho \leq 0.02E - 1.4 \quad (1)$$

wherein E is a tensile elongation in % of the film which is measured according to JIS K 7127.

Patentansprüche

1. Harzzusammensetzung, umfassend

(A) ein thermoplastisches Harz und Kohlenstofffüller,

wobei die Kohlenstofffüller aus Folgendem bestehen:

(B) Kohlenstoffnanoröhren; und
(C) Azetylenruß;

und optional auch (D) Kohlenstofffaser einschließen,
wobei die Menge von Komponente (B) 1 bis 60 Teile nach Gewicht ist, relativ zu 100 Teilen nach Gewicht von Komponente (A); die Menge von Komponente (C) 1 bis 100 Teile nach Gewicht ist, relativ zu 100 Teilen nach Gewicht von Komponente (A); und, wenn vorhanden, die Menge von Komponente (D) 1 bis 60 Teile nach Gewicht ist, relativ zu 100 Teilen nach Gewicht von Komponente (A).

2. Harzzusammensetzung nach Anspruch 1, wobei Komponente (A) mindestens eine, ausgewählt aus der Gruppe, bestehend aus Polyethylenen und chlorierten Polyethylenen, ist.

3. Harzzusammensetzung nach Anspruch 1 oder 2, wobei die Zusammensetzung ferner Folgendes umfasst:

(D) Kohlenstofffaser als einen Kohlenstofffüller.

4. Harzzusammensetzung nach einem der Ansprüche 1 bis 3, wobei die Menge von Komponente (B) 20 bis 60 Teile nach Gewicht ist, relativ zu 100 Teilen nach Gewicht von Komponente (A).

5. Harzzusammensetzung nach Anspruch 4, wobei die Menge von Komponente (B) 20 bis 50 Teile nach Gewicht ist, relativ zu 100 Teilen nach Gewicht von Komponente (A).

6. Verwendung der Harzzusammensetzung nach einem der Ansprüche 1 bis 5, wobei die Zusammensetzung für eine Elektrode einer Redox-Fluss-Batterie zu verwenden ist.

7. Elektrisch leitende Harzfolie, umfassend die Harzzusammensetzung nach einem der Ansprüche 1 bis 5.

8. Elektrisch leitende Harzfolie nach Anspruch 7, wobei die Folie einen Volumenwiderstand in $\Omega \cdot \text{cm}$, p , gemessen gemäß JIS K 7194, von $10 \Omega \cdot \text{cm}$ oder weniger hat und der Volumenwiderstand, p , folgende Gleichung (1) erfüllt:

$$\text{Log } p \leq 0,02 E - 1,4 \quad (1)$$

wobei E eine Zugausdehnung in % der Folie ist, die gemäß JIS K 7127 gemessen wird.

Revendications

1. Composition de résine comprenant :

(A) une résine thermoplastique et des charges de carbone,

dans laquelle les charges de carbone sont constituées par ce qui suit :

(B) des nanotubes de carbone ; et
(C) du noir d'acétylène ;

et, optionnellement, incluent également (D) de la fibre de carbone,
dans laquelle la quantité du composant (B) est de 1 à 60 partie (s) en poids, par rapport à 100 parties en poids du

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composant (A) ; la quantité du composant (C) est de 1 à 100 partie (s) en poids, par rapport à 100 parties en poids du composant (A) ; et, lorsqu'il est présent, la quantité du composant (D) est de 1 à 60 partie(s) en poids, par rapport à 100 parties en poids du composant (A).

2. Composition de résine selon la revendication 1, dans laquelle le composant (A) est au moins un composant qui est sélectionné parmi le groupe constitué de polyéthylènes et polyéthylènes chlorés.

3. Composition de résine selon la revendication 1 ou 2, dans laquelle la composition inclut en outre :

(D) de la fibre de carbone en tant que charge de carbone.

4. Composition de résine selon l'une quelconque des revendications 1 à 3, dans laquelle la quantité du composant (B) est de 20 à 60 parties en poids, par rapport à 100 parties en poids du composant (A).

5. Composition de résine selon la revendication 4, dans laquelle la quantité du composant (B) est de 20 à 50 parties en poids, par rapport à 100 parties en poids du composant (A).

6. Utilisation de la composition de résine selon l'une quelconque des revendications 1 à 5, dans laquelle la composition est destinée à être utilisée pour une électrode d'une batterie à flux redox.

7. Film en résine électriquement conducteur comprenant la composition de résine selon l'une quelconque des revendications 1 à 5.

8. Film en résine électriquement conducteur selon la revendication 7, dans lequel le film présente une résistivité volumique en $\Omega \cdot \text{cm}$, ρ , mesurée conformément à JIS K 7194, de 10 $\Omega \cdot \text{cm}$ ou moins, et la résistivité volumique, ρ , satisfait l'équation (1) qui suit :

$$\text{Log } \rho \leq 0,02 E - 1,4 \quad (1)$$

dans laquelle E est un allongement à la traction en % du film qui est mesuré conformément à JIS K 7127.

Fig.1

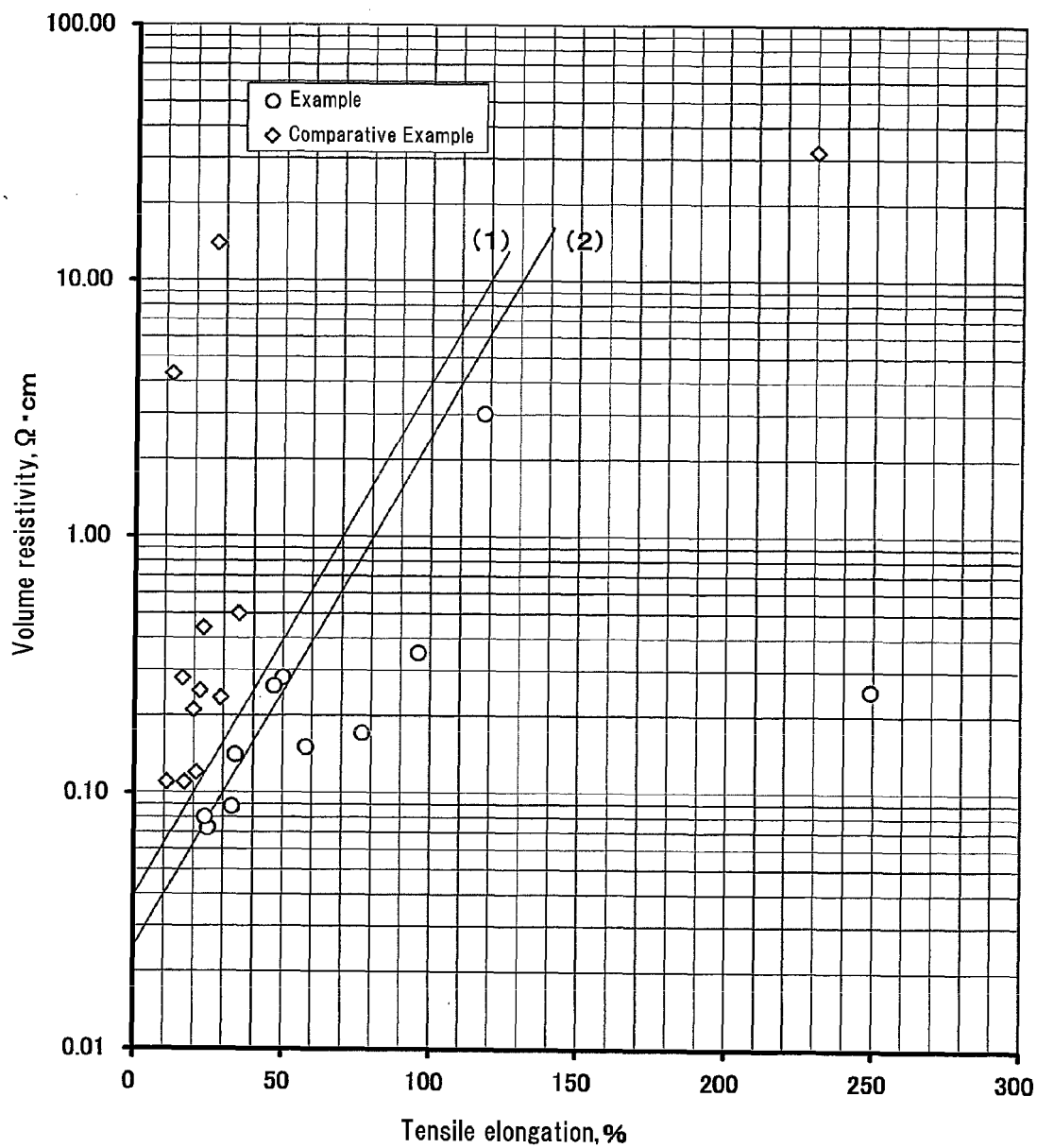


Fig. 1

REFERENCES CITED IN THE DESCRIPTION

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